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Thermal expansion studies on a metallic–glass ribbon-reinforced glass–ceramic-matrix composite

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The thermal-expansion behaviour of a metallic-glass ribbon-reinforced glass–ceramic-matrix composite was studied. The coefficient of thermal expansion of such composites measured in the longitudinal direction was correlated with the volume fraction, the length and the width of the ribbon reinforcements. The experimentally measured values of the thermal-expansion coefficients were found to be in good agreement with a modified Schapery's equation. Formation of an oxide layer on the ribbon surface and other related phenomena occurring at elevated temperatures were also found to affect the thermal expansion of such composites, and these factors were accommodated into Schapery's equation by incorporating an empirical constant.

1. Introduction

Metallic-glass reinforced-metal [1] and polymer-matrix [2–5] composites have been found to exhibit superior mechanical properties. The potential of using metallic-glass ribbons as reinforcements for a glass–ceramic matrix has also been demonstrated [6–13]. Very small volume fractions of metallic-glass reinforcements incorporated into a glass–ceramic matrix were found to significantly improve the strength and toughness of the brittle glass–ceramic at room temperature. The elevated-temperature properties and load-transfer characteristics in such a ribbon-reinforced system have also been studied and were found to be strongly dependent on the interfacial bonding between the ribbon and the matrix. The role of the interface and its effect on the failure mode of such a composite at various temperatures has also been investigated [8]. The formation of an oxide layer on the ribbon surface at elevated temperatures has been found to be primarily responsible for a reduction in the interfacial bonding between the ribbons and the matrix, which in turn is conducive to increased fracture-energy absorption and toughness [8].

The thermal-expansion behaviour of such composites needs to be investigated if they are to be used in elevated-temperature structural applications. The thermal expansion is of critical importance in design considerations, and it can dictate important parameters such as the component size and shape. The thermal-expansion behaviour can also be correlated to the interfacial bonding and critical length of the reinforcement [14], and in turn, it can be used in conjunction with other techniques of mechanical-property characterization.

In the present study, the thermal expansion of continuous and discontinuous metallic-glass ribbon-reinforced glass–ceramic-matrix composites was measured. The experimentally measured thermal-expansion values were compared with those predicted by Schapery's model [15]. The effect of the ribbon volume fraction and the ribbon dimensions (length and width) on the composite expansion was investigated. The effect of ribbon surface oxidation on the overall composite expansion was studied and the results obtained were correlated with the overall mechanical behaviour of the composite.

2. Experimental Procedure

Metglas ®2605 S-2 was used as the reinforcement in the present study. The metallic-glass ribbons, 2 inches wide with an average thickness of 25 μm were obtained from Metglas Corporation in the form of continuous spools. Corning glass 7572 was used as the starting matrix material. The physical properties and chemical composition of the ribbon and matrix are provided in Tables I and II, respectively. Specimens were fabricated in a steel die using conventional wet-pressing techniques with amyl acetate as the binder. Binder burn-out at 200 °C, was followed by a sintering step at 400 °C, and a devitrification step at 450 °C. Details of the specimen fabrication process are provided elsewhere [8].

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TABLE I Properties of the metallic-glass ribbon (as specified by the manufacturer Metglas Corporation).

Property	Metglas 2605S-2
Chemical composition	Fe 78% B 13% Si 9%
Crystallization temperature	550 °C
Elastic modulus	85 GPa
Yield strength	1200 MPa
Coefficient of thermal expansion	$7.6 \times 10^{-6}\,°\mathrm{C}^{-1}$
Density	$7180\,\mathrm{kg\,m^{-3}}$

TABLE II Properties of the glass matrix (as specified by the manufacturer Corning Inc.).

Property		Corning Code 7572
Chemical composition		PbO 70% ZnO 15% B_2O_3 5% SiO_2 5% Al_2O_3 5%
Softening temperature		375 °C
Coefficient of thermal expansion		$9.5 \times 10^{-6}\,°\mathrm{C}$
Density	powder	$3800\,\mathrm{kg\,m^{-3}}$
	fired	$6000\,\mathrm{kg\,m^{-3}}$

Thermal-expansion measurements were made on rectangular bar-shaped samples, with an Orton dilatometer (Model 1000 D) according to ASTM Standard C-372/81. The dilatometer was interfaced with a computer which was used to calculate and record the expansion data. A sample length of 2.54 ± 0.3 cm was used in all the tests. The thermal expansion of the samples was detected by a linear variable differential transducer (LVDT) system with a resolution of $\pm 0.25\%$ in the LVDT range of ± 0.318 cm and a repeatability of 65×10^{-4} cm. All of the expansion measurements were carried out in air. A heating rate of $3\,°\mathrm{C\,min^{-1}}$ was used in these measurements.

In order to examine the effect of ribbon surface oxidation, the samples were heated to various temperatures (250, 300, 350, 400 and 450 °C) and held at those temperatures for 15, 30, 45, 60, 90 and 120 min. These time intervals were chosen on the basis of experimental considerations (specimen sintering was usually carried out by heating the samples to 400 °C for 90 min followed by a devitrification step at 450 °C for 30–90 min). The thermal expansion (measured in an interval of + 10 °C of the actual test temperature) of the samples was measured by heating the samples quickly ($10\,°\mathrm{C\,min^{-1}}$) to these temperatures, and holding them at these temperatures for at least 10–15 min to equalize the temperature within the samples. The higher rate of heating was used to minimize the effects of additional exposure at these elevated temperatures.

3. Results and discussion

The following expression, due to Schapery [15] can be used to predict the coefficient of thermal expansion (CTE) of a ribbon-reinforced composite in the longitudinal direction

$$\alpha_L = \frac{E_m \alpha_m V_m + E_r \alpha_r V_r}{E_m V_m + E_r V_r} \qquad (1)$$

where E is Young's modulus, V is the volume fraction, and α is the coefficient of thermal expansion. The subscripts L, m and r denote properties of the composite in the longitudinal direction, in the matrix and in the ribbon, respectively. This equation assumes perfect mechanical bonding between the continuous reinforcement and the matrix, with no chemical interaction between the two.

Studies have been carried out to describe the relationship between mechanical properties such as modulus and strength, and the length of the reinforcement in fibrous composites [16, 17]. The thermal expansion of such a composite is affected by the shear transfer process at the interface in a manner similar to that experienced by a mechanical strain. Using this analogy, and extending the concept to a ribbon reinforcement, Schapery's equation can be modified for discontinuous ribbons by introducing the empirical constants K_L (for the length) and K_W (for the width) by

$$\alpha_L = \frac{E_m \alpha_m V_m + K_L K_W E_r \alpha_r V_r}{E_m V_m + K_L K_W E_r V_r} \qquad (2)$$

Here K_L and K_W satisfy the condition $0 \leqslant K_L K_W \leqslant 1$. These two constants are not independent of each other because the critical ribbon length has been shown to be dependent on the ribbon width [11].

The values of K_L and K_W were evaluated empirically for the composites containing discontinuous ribbon reinforcements using Equation 2. For a maximum ribbon length of 4 cm (the maximum possible based on experimental considerations), the value of K_L can be taken as equal to 1. Substituting this value and values for the other constants in Equation 2, the values of K_W for the ribbon widths of 0.25 and 0.5 cm were evaluated. These values were then used to obtain K_L for the other ribbon lengths of 1.0 and 0.5 cm, respectively. A summary of the empirical constants evaluated is provided in Table III.

The effect of varying the ribbon length and width (for the same volume fraction) on the CTE of the composite can be seen from the data in Tables IV and V, respectively. Decreasing the ribbon length, while keeping the ribbon width the same, for a given volume fraction, was found to increase the total expansion of the composite. The experimental value of the CTE has

TABLE III The empirically determined constants K_L and K_W for different ribbon lengths and widths (volume fraction of ribbons $V_r = 5.8\%$)

Ribbon length, L_r (cm)	Ribbon width, W_r (cm)	K_W	K_L
4.0	0.5	0.669	1.0
4.0	0.25	0.438	1.0
1.0	0.5	0.669	1.153
1.0	0.25	0.438	1.153
0.5	0.5	0.669	1.629

TABLE IV The effect of the ribbon length on the thermal expansion of the composite (volume fraction of the ribbons $V_r = 5.8\%$)

Ribbon length, L_r (cm)	Ribbon width, W_r (cm)	$\frac{L_r}{L_{composite}}$	$\frac{\alpha_{exp}}{\alpha_{theor\ (mod)}}$	$\frac{\alpha_{exp}}{\alpha_{theor\ (unmod)}}$
0.5	0.5	0.12	1.02	0.82
1.0	0.5	0.25	0.996	0.84
4.0	0.5	1.0	0.987	0.87

TABLE V The effect of the ribbon width on the thermal expansion of the composite (volume fraction of ribbons $V_r = 5.8\%$)

Ribbon length, L_r (cm)	Ribbon width, W_r (cm)	$\frac{L_r}{L_{composite}}$	$\frac{\alpha_{exp}}{\alpha_{theor\ (mod)}}$	$\frac{\alpha_{exp}}{\alpha_{theor\ (unmod)}}$
4.0	0.5	1.0	0.987	0.87
4.0	0.25	1.0	1.13	0.85
1.0	0.5	0.25	0.996	0.84
1.0	0.25	0.25	1.06	0.832

been compared with the values predicted by the original Schapery equation (Equation 1) and by the modified Schapery equation (Equation 2). The experimental values agreed more closely with the values predicted by the modified Schapery equation.

Experimentally observed values of the CTE, for increasing volume fractions of the reinforcement (of a given size), are provided in Table VI. Increasing the volume fraction of the reinforcements decreased the overall CTE of the composite. This is not unexpected because the ribbons have a smaller CTE than the matrix.

In all of the above calculations provided so far, the interface has been assumed to be unaffected by the thermal effects. The ribbons and the matrix were assumed to be perfectly bonded to one another at the test temperature. Studies carried out previously [12, 13] have indicated that strong bonding exists between the ribbons and the matrix in the as-fabricated state. Micrographs illustrating the nature of the bonding between the ribbons and matrix are provided in Fig. 1a and b. However, temperature has been shown to have a significant effect on the interfacial strength in such composites. We have shown previously that the interfacial strength decreases significantly above 250 °C [12, 13]. This decrease in the interfacial bonding strength was due to the formation of a non-adherent oxide layer on the ribbon surface, and it was responsible for a change in the failure mode of the composite. Multiple matrix cracking was obtained in the presence of the oxide layer on the ribbon surface, whereas single matrix cracks were obtained when there was no oxide layer present on the ribbon surface. The samples which exhibited multiple matrix cracks showed increased energy absorption during failure and a correspondingly higher fracture toughness.

Results of the measured composite expansion as a function of different exposure times at elevated temperatures are given in Table VII. With increasing temperature, the overall composite CTE increases.

TABLE VI The effect of the volume fraction of ribbons on the thermal expansion of the composite (ribbon length, $L_r = 4.0$ cm, and ribbon width, $W_r = 0.5$ cm)

Volume fractions of ribbons (%)	$\alpha_{experimental}$ $(10^{-6}\,{}^{\circ}C^{-1})$	$\frac{\alpha_{exp}}{\alpha_{theor\ (mod)}}$	$\frac{\alpha_{exp}}{\alpha_{theor\ (unmod)}}$
0.0	9.83	1.03	1.03
0.8	9.29	1.02	0.97
2.0	9.01	0.98	0.93
2.5	9.00	0.98	0.92
3.5	9.16	1.00	0.93
5.8	8.94	0.99	0.87
100	7.10	0.93	0.93

Formation of the oxide layer on the surface of the ribbon is believed to reduce the bonding between the matrix and the reinforcement, and subsequently to reduce the restraint by the ribbons on the matrix.

This effect of the interfacial bonding on the composite CTE can be accommodated into the Schapery equations by introducing another empirical constant, K_i. The subscript i denotes the interface effects. Since the interface controls the load transfer between the ribbons and matrix, the effect of the interface can be incorporated into the Schapery equation. The equation describing the longitudinal thermal-expansion coefficient of the composites can then be written as

$$\alpha_L = \frac{E_m \alpha_m V_m + K_L K_W K_i E_r \alpha_r V_r}{E_m V_m + K_L K_W K_i E_r V_r} \qquad (3)$$

Here, $0 \leqslant K_L K_W K_i \leqslant 1$.

In Equation 3, the volume fraction of the oxide layer, which was found to be relatively small (less than 0.1%), is ignored. The values of K_i, determined empirically from Equation 3 are given in Table VII. The values of K_i decreased with increasing temperatures. This decrease can be associated with the beginning of the formation of the oxide layer on the ribbon surface; this is enhanced at elevated temperatures.

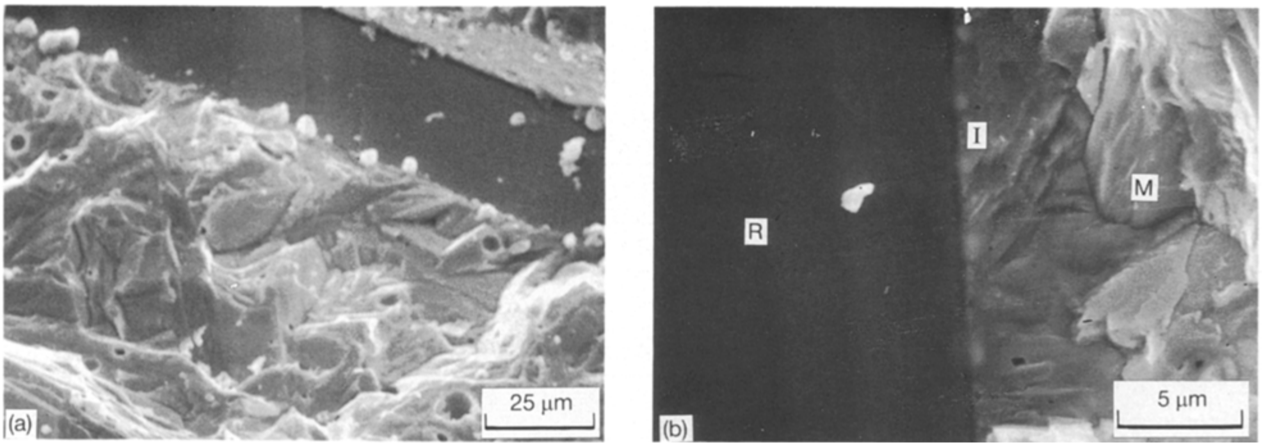


Figure 1 Scanning micrographs of the fractured surface of the metallic-glass ribbon-reinforced glass–ceramic-matrix composite in the as-fabricated state illustrating nature of the bonding between the reinforcement and matrix. R denotes the ribbon, M denotes the matrix, and I denotes the interface. (a) A strong continuous bond. (b) The absence of ribbon/matrix debonding.

TABLE VII The effect of temperature and time on the thermal expansion of the composite (ribbon volume fraction $V_r = 5.8\%$, ribbon length $L_r = 4.0$ cm, and ribbon width $W_r = 0.5$ cm)

Temperature (°C)	Time (min)	$\frac{\alpha_{\text{exp}}}{\alpha_{\text{theor (mod)}}}$	K_i
250	15	0.967	1.460
	30	0.954	1.656
	45	0.961	1.413
	60	0.948	1.624
	90	0.947	1.833
	120	0.963	1.843
300	15	0.958	1.196
	30	0.963	1.678
	45	0.971	1.789
	60	0.983	1.855
	90	0.991	1.767
	120	0.987	1.855
350	15	0.993	1.101
	30	1.019	1.616
	45	1.021	1.657
	60	0.983	0.902
	90	0.997	1.180
	120	0.999	1.22
400	15	0.998	0.404
	30	1.123	0.505
	45	1.028	0.648
	60	1.031	0.902
	90	1.027	1.060
	120	1.031	0.981
450	15	1.011	0.582
	30	1.121	0.318
	45	1.210	0.465
	60	1.070	0.206
	90	1.030	0.201
	120	0.98	0.505

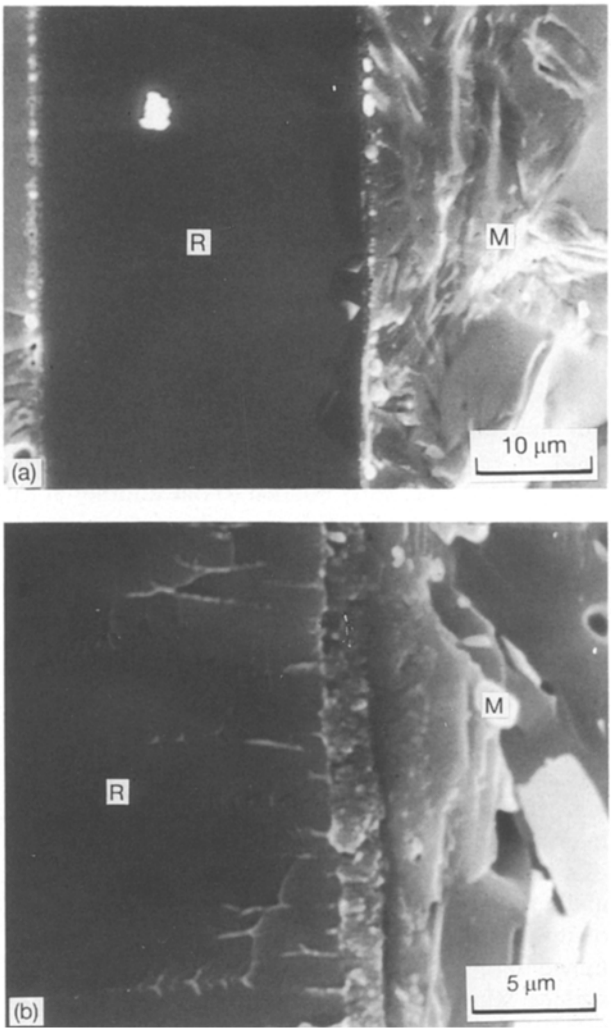
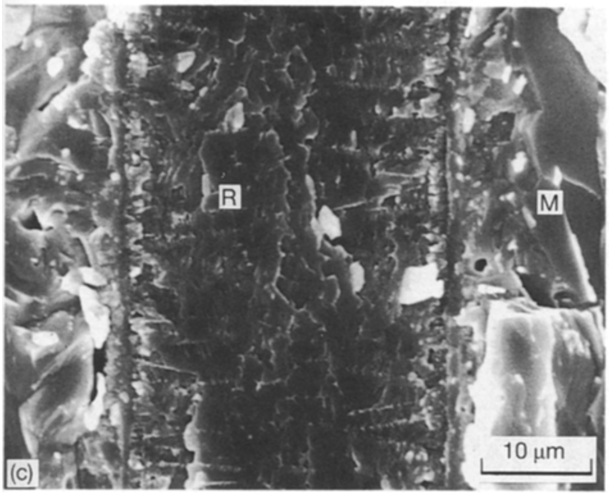


Figure 2 Scanning micrographs of the fractured surfaces of the metallic-glass ribbon-reinforced glass–ceramic matrix composite illustrating the changes at the interface with temperature. R denotes the ribbon, M denotes the matrix, and I denotes the interface. (a) 250 °C, 120 min, showing the beginning of the formation of an oxide layer on the ribbon surface. (b) 350 °C, 120 min, showing the increased thickness of the oxide layer. (c) 450 °C, 120 min, showing oxide layer formation and crystallization of the entire ribbon surface.

The effect of increasing exposure times at elevated temperatures, on the interface can be seen from the micrographs Fig. 2. The surface of the ribbon begins to oxidize to some degree even at 250 °C. However, significant oxide layer formation only begins at temperatures above 300 °C. At these temperatures the oxide layer on the ribbon surface is clearly visible.



Increasing the time of exposure at elevated temperatures causes a growth in the oxide layer. The oxide layer formed on the surface of the ribbons is relatively brittle and non-adherent. Further exposure to elevated temperatures leads to the diffusion of lead and zinc from the matrix to the ribbon, which in turn promotes crystallization of the amorphous ribbon. This process is more pronounced at elevated temperatures. This crystallization of the ribbons is undesirable, as it degrades the mechanical strength of the composites. Further studies to minimize and prevent such a phenomenon from occurring by the use of ribbon coatings, are in progress.

These studies have demonstrated the possibility of predicting the CTE of metal-ribbon-reinforced glass–ceramic-matrix composites. The constants utilized in the present analysis need to be determined empirically, and then used judiciously.

4. Conclusion

The thermal expansion of metallic-glass ribbon-reinforced glass–ceramic-matrix composites can be predicted by using the Schapery equation in a modified form. The empirical constants introduced in the equation can accommodate varying ribbon lengths and widths. The effect of changing interfacial characteristics can also be accounted for by incorporating another empirical constant.

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